

# Disorder effects on the static scattering function of star branched polymers

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We present analysis of the impact of structural disorder on the static scattering function of  $f$ -armed star branched polymers in  $d$  dimensions. To this end, we consider the model of a star polymer immersed in a good solvent in presence of structural defects, correlated on large distances  $r$  according to a power law  $\sim r^{-a}$ . In particular, we are interested in the ratio  $g(f)$  of scattering intensities of star and linear polymers of the same molecular weight, which is a universal experimentally measurable quantity. We apply the direct polymer renormalization approach and evaluate results within the double  $\varepsilon = 4 - d$ ,  $\delta = 4 - a$ -expansion. We find an increase of  $g(f)$  with increasing  $\delta$ . Therefore, an increase of disorder correlations leads to decrease of distinction between the size measure of a star and linear polymers of the same molecular weight.

**Key words:** *polymers, structural disorder, universality, renormalization group*

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## 1. Introduction

Scattering experiments are commonly used in investigations of the structure properties of condensed matter for more than a century (see, e.g. [1]). For polymer systems, the quantity of interest is the static structure function  $S(k)$  as function of the wave vector  $\vec{k}$ , representing the Fourier transform of the monomer-monomer correlation function [2–7]. The scattering intensity  $I(k) \equiv S(k)/S(0)$  at small  $k$  gives the radius of gyration  $R_g$  of a single macromolecule:

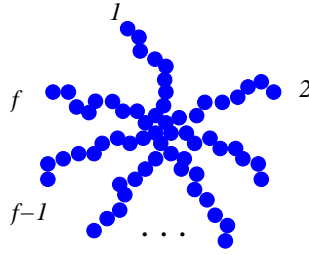
$$I(k) = 1 - k^2 \frac{\langle R_g^2 \rangle}{d} + \dots, \quad (1.1)$$

where  $d$  is the space dimension and  $\langle \dots \rangle$  denotes average over the ensemble of all conformations, the macromolecule in a solvent may attain.

In this paper, we intend to derive some theoretical predictions and quantitative description on the peculiarities of scattering experiments with star-like polymers. The star-like polymers are the simplest representatives of the class of branched polymer structures, being in a close relationship to complex systems such as gel, rubber, micellar and other polymeric and surfactant systems [8–10]. In particular, some conformational properties of star polymers could be easily generalized to determine the behavior of polymer networks of more complicated structure [11, 12]. The star polymer can be viewed as  $f$  linear polymer chains (arms) linked together at the central core (see Fig. 1). For  $f = 1(2)$  one restores the polymer chain of linear architecture, whereas it has been shown that in another limiting situation ( $f \gg 1$ ) the star polymer attains the features of soft colloidal particle [13].

A convenient parameter for comparing the size measure of a star consisting of  $f$  arms (each of lengths  $N$ ) and a linear polymer chain having the same molecular weight  $fN$  is the ratio:

$$g(f) \equiv \frac{\langle R_{g\text{star}}^2 \rangle}{\langle R_{g\text{chain}}^2 \rangle}, \quad (1.2)$$



**Figure 1.** Schematic presentation of an  $f$ -armed star polymer.

here  $\langle R_{g\text{star}}^2 \rangle$  is the mean square radius of gyration of the star polymer. Note, that the value (1.2) is an experimentally measurable quantity. Indeed, recalling (1.1) one has at small  $k$ :

$$\frac{I(k)_{\text{star}} - 1}{I(k)_{\text{chain}} - 1} = g(f) + \dots \quad (1.3)$$

Therefore, comparing the values of the corresponding scattering intensities at the same value of the wave vector allows to define the  $g(f)$  ratio experimentally. Moreover, it is well established, that the gyration radius of a star polymer scales with its total number of segments according to the scaling law:

$$\langle R_{g\text{star}}^2 \rangle \sim (fN)^{2\nu}, \quad (1.4)$$

with an universal exponent  $\nu$  that also governs the scaling of a single polymer chain of  $N$  monomers:  $\langle R_{g\text{chain}}^2 \rangle \sim N^{2\nu}$ . Therefore, the ratio  $g(f)$  of a star and linear chain of the same total molecular weight is  $N$ -independent.

In the pioneering work of Zimm and Stockmayer [14], an estimate for the size ratio  $g(f)$  was found analytically:

$$g(f) = \frac{3f - 2}{f^2}. \quad (1.5)$$

Inserting  $f = 1$  or  $f = 2$  in this relation, one restores the trivial result  $g = 1$ . For any  $f \geq 3$ , ratio (1.5) is smaller than 1, reflecting the fact that the size of a branched polymer is always smaller than the size of a linear polymer chain of the same molecular weight. Note that in deriving the expression (1.5) the excluded volume effect was neglected (restricting to the idealized Gaussian case, where (1.4) holds with size exponent  $\nu = 1/2$ ). In this limit the result holds for any space dimension. Dimensional dependence of the size ratio  $g(f)$  is found introducing the concept of excluded volume, applied to polymer macromolecules by P. Flory. It refers to the idea that any segment (monomer) of macromolecule may not occupy space that is simultaneously occupied by another segment; this causes a swelling of a polymer in solution with size exponent  $\nu(d) \geq 1/2$ . Later analytical [15–17] and numerical [18–22] studies have found the value of  $g(f)$  to increase if the excluded volume effect is taken into consideration.

While reliable estimates are known for the value of  $g(f)$  for polymers in a good solvent, there are no similar estimates for the case when the polymer is immersed in a good solvent at presence of structural impurities or a porous environment. However, such estimates are of a great importance for an understanding of the behavior of macromolecules in colloidal solutions [23] or near microporous membranes [24]. The density fluctuations of such obstacles lead to a large spatial inhomogeneities, which often produce pore-like fractal structures [25]. Such a disordered (porous) environment may be found, in particular, in a biological cell, composed of many different kinds of biochemical species [26]. It has been proven both analytically [27] and numerically [28], that the presence of uncorrelated point-like defects of weak concentration does not change the universality class of polymers. Here, however, we address a case, where the structural obstacles of the environment are spatially correlated on a mesoscopic scale [29]. Following Ref. [30], this case may be described by assuming the defects to be correlated on large distances  $r$  according to a power law

resulting in a pair correlation function:

$$h(r) \sim r^{-a}. \quad (1.6)$$

For  $a < d$ , specific situations giving rise to such a correlation function include defects extended in space e.g. the cases  $a = d - 1$  ( $a = d - 2$ ) may be represented by lines (planes) of defects of random orientation, whereas non-integer values of  $a$  may include obstacles of fractal structures (see [30, 31] for further details). The impact of long-range-correlated disorder on the scaling of linear and star branched polymers has been analyzed in previous works [31] by means of the field-theoretical renormalization group (RG) approach. The aim of the present paper is to evaluate analytically an experimentally measurable ratio (1.3) for a star polymer in a solvent in the presence of structural defects correlated according to (1.6).

The layout of the reminder of the paper is as follows. In the next section, we develop a description of the problem in the frames of the Edwards continuous chain model. In section III, the direct polymer renormalization method is briefly described; the results of its application to the problem under consideration are presented in Section IV. Conclusions and an outlook are given in Section V.

## 2. The model

We consider star polymers with  $f$  arms in a solution in the presence of structural obstacles. In the frames of the Edwards continuous chain model [1], each arm of the star is presented by a path  $r_i(s)$ , parameterized by  $0 \leq s \leq S_i$ ,  $i = 1, 2, \dots, f$ . The central branching point of the star is fixed in space, so that:  $\vec{r}_1(0) = \dots = \vec{r}_f(0) = 0$ . We take the contour length of all arms to be equal:  $S_1 = \dots = S_f = S$ . The partition function of the system reads:

$$\begin{aligned} Z_f(S) = \int \mathcal{D}\{r\} \prod_{i=1}^f \delta(\vec{r}_i(0)) \exp \left[ -\frac{1}{2} \sum_{i=1}^f \int_0^S ds \left( \frac{d\vec{r}_i(s)}{ds} \right)^2 - \right. \\ \left. -\frac{b_0}{2} \sum_{i,j=1}^f \int_0^S ds' \int_0^S ds'' \delta(\vec{r}_i(s'') - \vec{r}_j(s')) + \sum_{i=1}^f \int_0^S ds V(\vec{r}_i(s)) \right]. \end{aligned} \quad (2.1)$$

Here, a multiple path integral is performed for the paths  $r_1, \dots, r_f$  and the product of  $\delta$ -functions reflects the star-like configuration of  $f$  chains. The first term in the exponent represents the chain connectivity, the second term describes the short range excluded volume interaction with bare coupling constant  $b_0$ , and the last term contains random potential  $V(\vec{r}_i(s))$  arising due to the presence of structural disorder. Denoting by  $\overline{(\dots)}$  the average over different realizations of disorder, the first moment of the distribution is:

$$\overline{V(\vec{r}(s))} = \rho_0$$

with  $\rho_0$  being the density of obstacles. Let us introduce the notation for the second moment:

$$\overline{V(\vec{r}(s))V(\vec{r}(s'))} \equiv h(\vec{r}(s) - \vec{r}(s')). \quad (2.2)$$

Note that dealing with systems that display randomness of structure, one usually encounters two types of ensemble averaging, treated as quenched and annealed disorder [32]. The annealed case amounts to averaging the partition sum of the system over the random variables, whereas in the quenched case the free energy (or the logarithm of the partition sum) is to be averaged; the replica formalism is usually exploited in the last situation. In principle, the behavior of systems with quenched and annealed disorder is quite different. However, as has been shown in a number of works [33–36], *the distinction between quenched and annealed averages for an infinitely long single polymer chain is negligible*, and in performing analytical calculations for quenched polymer systems one may thus restrict the problem to the simpler case of annealed averaging. To average

the partition function of the system over different realizations of obstacles, we make use of the relation:

$$\overline{e^{ax}} = \exp \left( \sum_{n=1}^{\infty} \frac{a^n M_n(x)}{n!} \right), \quad (2.3)$$

where  $M_n(x)$  are  $n$ th cumulants of the random variable  $x$ :  $M_1(x) = \bar{x}$ ,  $M_2(x) = \overline{(x - \bar{x})^2}$  etc. Noticing that only the last term in (2.1) contains random variables and taking into account (2.2), we obtain:

$$\overline{\mathcal{Z}_f(S)} = \int \mathcal{D}\{r\} \prod_{i=1}^f \delta(\vec{r}_i(0)) e^{-H_{\text{dis}}} \quad (2.4)$$

with an effective Hamiltonian:

$$\begin{aligned} H_{\text{dis}} = & \frac{1}{2} \sum_{i=1}^f \int_0^S ds \left( \frac{d\vec{r}_i(s)}{ds} \right)^2 + \frac{b_0}{2} \sum_{i,j=1}^f \int_0^S ds' \int_0^S ds'' \delta(\vec{r}_i(s'') - \vec{r}_j(s')) - \\ & - \frac{1}{2} \sum_{i=1}^f \int_0^S ds' \int_0^S ds'' h(\vec{r}_i(s'') - \vec{r}_j(s')) - \rho_0 f S - \frac{1}{2} \rho_0^2 f S^2. \end{aligned} \quad (2.5)$$

The last two terms in (2.5) correspond to a trivial constant shift which will be omitted in the following analysis. Note also, that in (2.5) we do not take into account terms generated by higher-order correlations of the type (2.2), for the problem under consideration these are irrelevant in the renormalization group sense.

The case of structural disorder in the form of point-like uncorrelated defects corresponds to  $h(\vec{r}(s'') - \vec{r}(s')) = v_0 \delta(\vec{r}(s'') - \vec{r}(s'))$  where  $v_0$  is some constant. One immediately reveals that in this case one can adsorb the effect of disorder into the excluded volume coupling constant passing to the coupling:  $b_0 \equiv b_0 - v_0$ . This conclusion was obtained for the case of polymers in quenched disorder by Kim [27] on the basis of a refined field-theoretical study; in the present case of annealed disorder this is a straightforward result.

We address the model where the structural obstacles are spatially correlated at large distances  $r$  according to (1.6). Taking into account that the Fourier transform of the correlation function at small  $k$  is related to its large- $r$  behaviour via:

$$h(|\vec{r}_i(s'') - \vec{r}_j(s')|) \cong |\vec{r}_i(s'') - \vec{r}_j(s')|^{-a} \cong w_0 \int dk k^{a-d} e^{i\vec{k}(\vec{r}_i(s'') - \vec{r}_j(s'))}, \quad (2.6)$$

one is left with a model with two couplings  $b_0$  and  $w_0$ . Note that coupling  $b_0$  must be positive, which corresponds to an effective mutual repulsion of the monomers due to the excluded volume effect. The coupling  $w_0$  is positive as results from the Fourier image of the correlation function.

Performing dimensional analysis for the terms in (2.5) one finds the dimensions of the couplings in terms of dimension of contour length  $S$ :  $[b_0] = [S]^{d_{b_0}}$ ,  $[w_0] = [S]^{d_{w_0}}$  with  $d_{b_0} = (4 - d)/2$ ,  $d_{w_0} = (4 - a)/2$ . The ‘‘upper critical’’ values of the space dimension ( $d_c = 4$ ) and the correlation parameter ( $a_c = 4$ ), at which the couplings are dimensionless, play an important role in the renormalization scheme, as outlined below.

### 3. The method

To study the universal properties of polymer macromolecules in solutions, it is convenient to apply the direct renormalization method, as developed by des Cloizeaux [1]. The efficiency of this approach comes on the one hand from its close relation to the concepts of field theory [38], and on another hand from providing a considerably simpler treatment of a variety of complex polymer systems.

In the asymptotic limit of an infinite linear measure of the continuous polymer curve (corresponding to an infinite number of configurations), one observes various divergences. All these divergences can be eliminated by introducing corresponding renormalization factors, directly associated with physical quantities. This postulates the existence of a limiting theory, describing sets of very long polymers.

As a first step within this theory, we consider the size measure of an  $f$ -arm star polymer, given by the mean square end-to-end distance of its individual arm. When evaluated in terms of a perturbation theory series in bare coupling constants  $\{\lambda_0\}$ , this reads:

$$\langle R_e^2 \rangle = \langle (\vec{r}(S) - \vec{r}(0))^2 \rangle = \chi_0(\{\lambda_0\})S. \quad (3.1)$$

Here, the averaging is performed with respect to a corresponding effective Hamiltonian, and  $\chi_0(\{\lambda_0\})$  is the so-called swelling factor, reflecting the impact of interactions on the effective size of the macromolecules. For the case of a Gaussian chain (all couplings  $\lambda_0 = 0$ ) one has  $\chi_0(\{0\}) = 1$ . Recalling the scaling of the polymer size with its molecular weight:

$$\langle R_e^2 \rangle \sim N^{2\nu} \sim S^{2\nu}, \quad (3.2)$$

one finds an estimate for the effective critical exponent  $\nu(\{\lambda_0\})$ :

$$2\nu(\{\lambda_0\}) - 1 = S \frac{\partial}{\partial S} \ln \chi_0(\{\lambda_0\}). \quad (3.3)$$

The second renormalization factor  $\chi_1(\{\lambda_0\})$  is introduced via:

$$\frac{\mathcal{Z}_f(S)}{\mathcal{Z}_f^0(S)} = [\chi_1(\{\lambda_0\})]^2. \quad (3.4)$$

Here,  $\mathcal{Z}_f(S)$  is the partition function of an  $f$ -arm star polymer and  $\mathcal{Z}_f^0(S)$  – the partition function of an idealized Gaussian model. It is established, that the number of all possible conformations of an  $f$ -armed star polymer scales with the weight of the macromolecule parametrised by  $S$  as:

$$\mathcal{Z}_f(S) \sim \mu^{fS} (fS)^{\gamma_f - 1}. \quad (3.5)$$

Here, the  $\gamma_f$  are additional universal critical exponents, depending only on the space dimension  $d$  and the number of arms  $f$  (exponents  $\gamma_1 = \gamma_2 \equiv \gamma$  restore the value for the single polymer chain),  $\mu$  is a non-universal fugacity. In similar way as for the size measure, one finds from the scaling assumption (3.5) an estimate for an effective critical exponent  $\gamma_f(\{\lambda_0\})$ , governing the scaling behavior of the number of possible configurations as:

$$\frac{\gamma_f(\{\lambda_0\}) - 1}{2} = S \frac{\partial \ln \chi_1(\{\lambda_0\})}{\partial S}. \quad (3.6)$$

The critical exponents (3.3) and (3.6), presented in the form of series expansions in the coupling constants  $\{\lambda_0\}$  are, however, divergent in the asymptotic limit of large  $S$ . To eliminate these divergences, the renormalization of the coupling constants is performed. Subsequently, the critical exponents attain finite values when evaluated at the stable fixed point (FP) of the renormalization group transformation. Note that the FP coordinates are universal, in particular the scaling of a single polymer chain and that of a polymer star is governed by the same unique FP. Therefore, to evaluate the FP coordinates in the following analysis we restrict ourselves to the simpler case of a single chain polymers ( $f = 1$ ). To define the coupling constant renormalization, one considers the second virial coefficient of a polymer solution, given by the relation:

$$\Pi\beta = C - \frac{1}{2}C^2 \sum_{\lambda_0} \frac{\mathcal{Z}_{\lambda_0}(S, S)}{[\mathcal{Z}_1(S)]^2} + \dots, \quad (3.7)$$

here,  $\Pi$  is the osmotic pressure,  $\beta = 1/k_B T$ ,  $C$  is the number of monomers per unit volume, and  $\mathcal{Z}_1(S)$  is the partition function of a single polymer chain.  $\mathcal{Z}_{\lambda_0}(S, S)$  are contributions into

partition function of two interacting chain polymers, having dimensions  $\mathcal{Z}_{\lambda_0}(S, S) \sim [S]^2[\lambda_0]$ . The renormalized coupling constants  $\lambda_R$  are thus defined by:

$$\lambda_R(\{\lambda_0\}) = -[\chi_1(\{\lambda_0\})]^{-4} Z_{\lambda_0}(L, L) [2\pi\chi_0(\{\lambda_0\}L)]^{-(2-d_{\lambda_0})}, \quad (3.8)$$

therefore:

$$\Pi\beta = C + \frac{1}{2} \sum_{\lambda_R} \lambda_R C^2 [2\pi\chi_0(\{\lambda_0\}L)]^{(2-d_{\lambda_0})} + \dots, \quad (3.9)$$

In the limit of infinite linear size of the macromolecules the renormalized theory remains finite, such that:

$$\lim_{S \rightarrow \infty} \lambda_R(\{\lambda_0\}) = \lambda_R^*. \quad (3.10)$$

Moreover, for negative  $d_{\lambda_0} \leq 0$  the macromolecules are expected to behave like Gaussian chains in spite of the interactions between monomers, thus each  $\lambda_R^* = 0$  for corresponding  $d_{\lambda_0} \leq 0$ . It is therefore proper to choose  $\{\lambda_R\}$  as expansion parameters, which remain finite for  $S \rightarrow \infty$  and which are also rather small close to the critical dimensions of the corresponding couplings. The concept of expansion around in small deviations from the upper critical dimensions of the coupling constants, thus naturally arises.

The flows of the renormalized coupling constants are governed by functions  $\beta_{\lambda_R}$ :

$$\beta_{\lambda_R} = 2S \frac{\partial \lambda_R(\{\lambda_0\})}{\partial S}. \quad (3.11)$$

Reexpressing  $\{\lambda_0\}$  in terms of renormalized couplings  $\lambda_R$  according to (3.8), consequently the fixed points of the renormalization group transformations are given by the common zeros of the  $\beta$ -functions. Stable fixed points govern the asymptotical scaling properties of macromolecules in solutions and allow e.g. to obtain reliable asymptotical values of the critical exponents (3.3) and (3.6).

## 4. Results

We start by evaluating the partition function (2.4) of the model with an effective Hamiltonian (2.5), performing an expansion in coupling constants  $b_0, w_0$ :

$$\begin{aligned} \overline{Z_f(S)} = \int \mathcal{D}r e^{-\frac{1}{2} \sum_{i=1}^f \int_0^S ds \left( \frac{d\vec{r}_i(s)}{ds} \right)^2} & \left( 1 - \frac{b_0}{2} \sum_{i,j=1}^f \int_0^S ds' \int_0^S ds'' \int d\vec{k} e^{i\vec{k}(\vec{r}_i(s'') - \vec{r}_j(s'))} \right. \\ & \left. + \frac{w_0}{2} \sum_{i,j=1}^f \int_0^S ds' \int_0^S ds'' \int d\vec{k} k^{a-d} e^{i\vec{k}(\vec{r}_i(s'') - \vec{r}_j(s'))} + \dots \right), \end{aligned} \quad (4.1)$$

here the Fourier-transform of  $\delta$ -function is exploited and the last term originates from the Fourier transform of the function  $h$  at small  $k$  (see Eq. (2.6)). Below, we will consider the one-loop approximation, keeping only the first-order terms in  $b_0, w_0$  in the expansions. One may rewrite:

$$e^{i\vec{k}(\vec{r}_i(s'') - \vec{r}_i(s'))} = \exp \left( i\vec{k} \int_{s'}^{s''} \frac{d\vec{r}_i(s)}{ds} ds \right), \quad (4.2)$$

$$e^{i\vec{k}(\vec{r}_i(s'') - \vec{r}_j(s'))} = \exp \left( i\vec{k} \int_0^{s''} \frac{d\vec{r}_i(s)}{ds} ds - i\vec{k} \int_0^{s'} \frac{d\vec{r}_j(s)}{ds} ds \right), \quad (4.3)$$

taking into account that  $r_i(0) = r_j(0) = 0$  in our model of a star-shaped polymer. Making use of the identity:

$$\exp \left[ -\frac{1}{2} \int_{s'}^{s''} ds \left( \frac{d\vec{r}_i(s)}{ds} \right)^2 + i\vec{k} \int_{s'}^{s''} \frac{d\vec{r}_i(s)}{ds} ds \right] = \exp \left[ -\frac{1}{2} \int_{s'}^{s''} ds \left( \left( \frac{d\vec{r}_i(s)}{ds} - i\vec{k} \right)^2 + k^2 \right) \right] \quad (4.4)$$

and taking into account that:

$$\int_{-\infty}^{\infty} dx e^{-A(x-ik)^2} = \int_{-\infty}^{\infty} dx e^{-Ax^2}, \quad (4.5)$$

we receive:

$$\begin{aligned} \overline{\mathcal{Z}_f(S)} = \mathcal{Z}_f^0(S) & \left[ 1 - b_0(2\pi)^{-\frac{d}{2}} \left( f \int_0^S ds'' \int_0^{s''} ds' (s'' - s')^{-d/2} + \right. \right. \\ & \left. \left. \frac{f(f-1)}{2} \int_0^S ds'' \int_0^S ds' (s' + s'')^{-d/2} \right) + \right. \\ & \left. w_0(2\pi)^{-\frac{a}{2}} \left( f \int_0^S ds'' \int_0^{s''} ds' (s'' - s')^{-a/2} + \frac{f(f-1)}{2} \int_0^S ds'' \int_0^S ds' (s' + s'')^{-a/2} \right) \right]. \quad (4.6) \end{aligned}$$

In the last equation, the Gaussian integration over  $k$  is performed and the notation  $\mathcal{Z}_f^0(S)$  is introduced for the partition function of “unperturbed” Gaussian model:

$$\mathcal{Z}_f^0(S) = \int \mathcal{D}r e^{-\frac{1}{2} \sum_{i=1}^f \int_0^S ds \left( \frac{dr_i(s)}{ds} \right)^2}. \quad (4.7)$$

In what follows, we will use the diagrammatic representation of the perturbation theory series (see Fig. 2). Performing the integrals in (4.6) and introducing dimensionless couplings

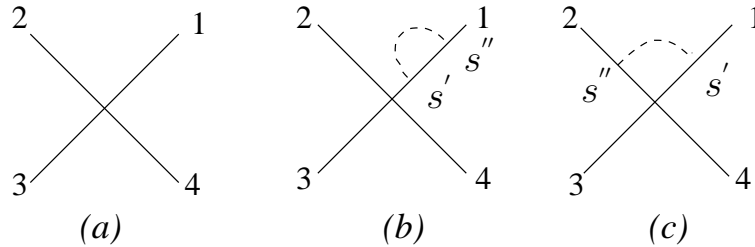
$$b = b_0(2\pi)^{-d/2} S^{2-d/2}, \quad w = w_0(2\pi)^{-a/2} S^{2-a/2} \quad (4.8)$$

we obtain:

$$\begin{aligned} \overline{\mathcal{Z}_f(S)} = \mathcal{Z}_f^0(S) & \left[ 1 - \frac{4b}{(2-d)(4-d)} \left( f + \frac{f(f-1)}{2} (2^{2-d/2} - 2) \right) + \right. \\ & \left. + \frac{4w}{(2-a)(4-a)} \left( f + \frac{f(f-1)}{2} (2^{2-a/2} - 2) \right) \right]. \quad (4.9) \end{aligned}$$

Finally, one may perform a double  $\varepsilon = 4 - d$ ,  $\delta = 4 - a$ -expansions:

$$\begin{aligned} \overline{\mathcal{Z}_f(S)} = 1 + b & \left( \frac{f(3-f)}{\varepsilon} + \frac{f(3-f)}{2} + \frac{f(f-1)}{2} \ln(2) \right) - \\ & - w \left( \frac{f(3-f)}{\delta} + \frac{f(3-f)}{2} + \frac{f(f-1)}{2} \ln(2) \right). \quad (4.10) \end{aligned}$$



**Figure 2.** Diagram contributions to the partition function of a 4-arm star up to the first order in the coupling constants. Dotted line denotes possible interactions between points  $s'$ ,  $s''$ , governed by couplings  $b_0$  and  $w_0$ . Integrations are to be performed over all positions of the segment end points i.e. over all mutual interaction points within a single arm and between different arms.

The averaged squared end-to-end distance  $\overline{\langle R_e^2 \rangle}$  of a single arm of a star polymer may be calculated using the identity:

$$\overline{\langle R_e^2 \rangle} = \overline{\langle (\vec{r}(S) - \vec{r}(0))^2 \rangle} = -2d \frac{\partial}{\partial q^2} \overline{\langle e^{i\vec{q}(\vec{r}(S) - \vec{r}(0))} \rangle} \Big|_{q=0} \quad (4.11)$$

where:

$$\overline{\langle \dots \rangle} = \frac{\int \mathcal{D}r e^{-\mathcal{H}_{\text{dis}}(\dots)} \prod_{i=1}^f \delta(\vec{r}_i(0))}{\mathcal{Z}_f(S)}. \quad (4.12)$$

Following the same scheme as described above for the partition function, we find:

$$\overline{\langle R_e^2 \rangle} = Sd \left( 1 + \frac{4b}{(4-d)(6-d)} - \frac{4w}{(4-a)(6-a)} \right). \quad (4.13)$$

We may therefore define a swelling factor  $\chi_0(b_0, w_0)$  (cf. (3.1)) as:

$$\chi_0(b_0, w_0) = \left( 1 + \frac{4b}{(4-d)(6-d)} - \frac{4w}{(4-a)(6-a)} \right) = \left( 1 + \frac{b}{\varepsilon}(2-\varepsilon) - \frac{w}{\delta}(2-\delta) \right). \quad (4.14)$$

Now we return to the calculation of the gyration radius. The gyration radius of a star polymer in a solvent in the presence of correlated defects may be written as:

$$\overline{\langle R_{g\text{star}}^2 \rangle} = \frac{1}{2(fS)^2} \int_0^S ds_1 \int_0^S ds_2 \overline{\left\langle \sum_{i,j=1}^f (\vec{r}_i(s_2) - \vec{r}_j(s_1))^2 \right\rangle}. \quad (4.15)$$

We rewrite:

$$\overline{\left\langle \sum_{i,j=1}^f (\vec{r}_i(s_2) - \vec{r}_j(s_1))^2 \right\rangle} = -2d \frac{\partial}{\partial |q|^2} \overline{\langle e^{i\vec{q} \sum_{i,j=1}^f (\vec{r}_i(s_2) - \vec{r}_j(s_1))} \rangle} \Big|_{q=0}, \quad (4.16)$$

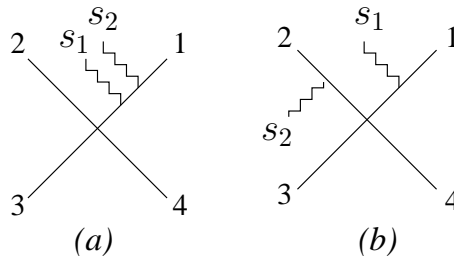
where  $d$  is the space dimension. First let us consider the zero-loop order of the expansion of (4.16) in coupling constants. A diagrammatic representation is given in Fig. 3. The analytic expression, corresponding to the diagram (a) reads:

$$f \overline{\langle e^{i\vec{q}(\vec{r}_1(s_2) - \vec{r}_1(s_1))} \rangle} = f e^{-\frac{q^2}{2}(s_2 - s_1)}, \quad (4.17)$$

whereas the diagram (b) gives:

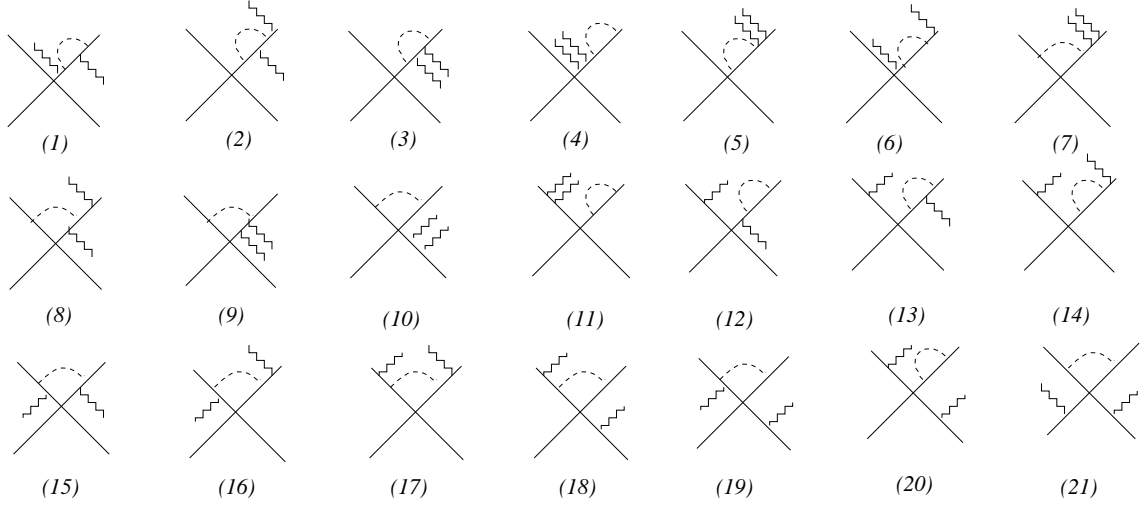
$$\frac{f(f-1)}{2} \overline{\langle e^{i\vec{q}(\vec{r}_2(s_2) - \vec{r}_1(s_1))} \rangle} = \frac{f(f-1)}{2} e^{-\frac{q^2}{2}(s_1 + s_2)}. \quad (4.18)$$

Note, that here and in what follows the Gaussian integral in (4.7) cancels against the numerator, when averaging (4.12) is performed. One thus distinguishes between two types of contributions:



**Figure 3.** Diagrammatic presentation of contributions into radius of gyration of star polymer in zeros order of perturbation theory.





**Figure 4.** Diagram contribution into the gyration radius at the one-loop level.

one resulting from insertions  $s_1, s_2$  along the same arm of the star, and the second corresponding to insertions located on two different arms. Taking the derivative with respect to  $q$ , and evaluating for  $q = 0$  according to (4.16), we have for the radius of gyration of a star polymer in the unperturbed (Gaussian) case:

$$\overline{\langle R_{g\text{star}}^2 \rangle} = \frac{d}{(fS)^2} \left[ f \int_0^S ds_2 \int_0^{s_2} ds_1 (s_2 - s_1) + \frac{f(f-1)}{2} \int_0^S ds_1 \int_0^S ds_2 (s_1 + s_2) \right] = \frac{dS}{f} \frac{3f-2}{6}. \quad (4.19)$$

Now, let us perform calculations up to the first order of the perturbation theory expansion in the couplings  $b_0, w_0$ . In Fig. 4, we present diagram contributions to (4.16), see Appendix for details. We have:

$$\begin{aligned} \overline{\left\langle \sum_{i,j=1}^f (\vec{r}_i(s_2) - \vec{r}_j(s_1))^2 \right\rangle} &= -2d \frac{\partial}{\partial q^2} \left[ f \left( I_1(d) + I_1(a) + I_2(d) + I_2(a) + I_3(d) + \right. \right. \\ &I_3(a) + I_4(d) + I_4(a) + I_5(d) + I_5(a) + I_6(d) + I_6(a) + I_7(d) + I_7(a) \Big) + \\ &\frac{f(f-1)}{2} (I_8(d) + I_8(a) + I_9(d) + I_9(a) + I_{10}(d) + I_{10}(a) + I_{11}(d) + I_{11}(a) + \\ &I_{12}(d) + I_{12}(a) + I_{13}(d) + I_{13}(a) + I_{14}(d) + I_{14}(a) + I_{15}(d) + I_{15}(a) + \\ &I_{16}(d) + I_{16}(a) + I_{17}(d) + I_{17}(a)) + \frac{f(f-1)(f-2)}{6} (I_{18}(d) + I_{18}(a) + \\ &I_{19}(d) + I_{19}(a) + I_{20}(d) + I_{20}(a)) + \left. \frac{f(f-1)(f-2)(f-3)}{24} (I_{21}(d) + I_{21}(a)) \right] \Big|_{q=0}. \quad (4.20) \end{aligned}$$

Here,  $I_i(d), I_i(a)$  are integrals listed in the Appendix. Performing the integration according to (4.15) and evaluating the double  $\varepsilon, \delta$ -expansion we find for the gyration radius:

$$\begin{aligned} \overline{\langle R_{g\text{star}}^2 \rangle} &= \frac{dS}{6f} (3f-2) \left[ 1 + b \frac{2}{\varepsilon} - w \frac{2}{\delta} - \right. \\ &\left. - (b-w) \left( \frac{13}{12} + \frac{13}{2} \frac{(f-1)(f-2)}{3f-2} - \ln(2) \frac{4(f-1)(3f-5)}{3f-2} \right) \right] \quad (4.21) \end{aligned}$$

The result for the radius of gyration of a single chain of total length  $fS$  is straightforward:

$$\begin{aligned}\overline{\langle R_{g\text{chain}}^2 \rangle} &= \frac{d(Sf)}{6} \left[ 1 + bf^{\varepsilon/2} \left( \frac{2}{\varepsilon} - \frac{13}{12} \right) - wf^{\delta/2} \left( \frac{2}{\delta} - \frac{13}{12} \right) \right] = \\ &= \frac{d(Sf)}{6} \left[ 1 + b \left( \frac{2}{\varepsilon} - \frac{13}{12} \right) - w \left( \frac{2}{\delta} - \frac{13}{12} \right) + (b-w) \ln(f) \right].\end{aligned}\quad (4.22)$$

Finally, we need to perform the renormalization of coupling constants. To this end, we need the contributions to the partition function  $\overline{Z(S, S)}$  of the system of two interacting polymer chains of the same length  $L$ . In the diagrammatic representation of this function, one takes only those terms into account, which contain at least one interaction line (see Fig. 5). In general, performing a thorough dimensional analysis of the contributions, produced by different diagrams, we find two distinct classes of the diagrams. The first class of graphs produces terms which behave as  $[S]^2[b_0]$ , the sum of all such terms contributes to the function denoted by  $\overline{Z_{b_0}(S, S)}$ ; the second class of diagrams behaves as  $[S]^2[w_0]$  and thus contributes to the function  $\overline{Z_{w_0}(S, S)}$ .

We find the contributions to functions  $\overline{Z_{b_0}(S, S)}$  and  $\overline{Z_{w_0}(S, S)}$  as:

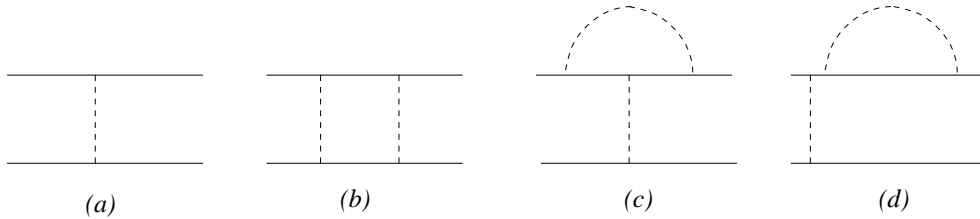
$$\begin{aligned}\overline{Z_{b_0}(S, S)} &= -b_0 S^2 \left( 1 - \frac{8b}{(2-d)(4-d)} + \frac{8w}{(2-a)(4-a)} - \right. \\ &\quad \left. \frac{32b}{(d-2)(d-4)(d-6)(d-8)} - \right. \\ &\quad \left. 32 \frac{w^2}{b} \frac{2a-d+2^{4-(2a-d)/2}-10}{(2a-d-2)(2a-d-4)(2a-d-6)(2a-d-8)} + \right. \\ &\quad \left. 64w \frac{a+2^{4-a/2}-10}{(a-2)(a-4)(a-6)(a-8)} \right), \\ \overline{Z_{w_0}(S, S)} &= w_0 S^2 \left( 1 - \frac{8b}{(2-d)(4-d)} + \frac{8w}{(2-a)(4-a)} \right).\end{aligned}\quad (4.23)$$

We may therefore define the dimensionless renormalized coupling constants  $b_R, w_R$  by (3.8):

$$\begin{aligned}b_R &= -\frac{\overline{Z_b(S, S)}}{\langle \overline{Z(S)} \rangle^2} [2\pi\chi_0(b_0, w_0)S]^{-\frac{d}{2}}, \\ w_R &= -\frac{\overline{Z_w(S, S)}}{\langle \overline{Z(S)} \rangle^2} [2\pi\chi_0(b_0, w_0)S]^{-\frac{a}{2}}.\end{aligned}\quad (4.24)$$

The RG flows of the renormalized coupling constants are governed by corresponding  $\beta$ -functions:

$$\beta_{b_R}(b, w) = 2S \frac{\partial b_R}{\partial S}, \quad \beta_{w_R}(b, w) = 2S \frac{\partial w_R}{\partial S}.\quad (4.25)$$



**Figure 5.** Diagrammatic presentation of contributions into the partition function of two interacting chains.

Reexpressing in (4.25)  $b$  and  $w$  in terms of the renormalized couplings (4.24), we finally have:

$$\begin{aligned}\beta_{b_R}(b_R, w_R) &= (4-d)b_R - b_R^2 \frac{2d}{6-d} + w_R b_R \frac{2d}{6-a} + 32b_R^2 \frac{d + 2^{4-d/2} - 10}{(d-2)(d-6)(d-8)} \\ &+ 32w_R^2 \frac{2a-d + 2^{4-(2a-d)/2} - 10}{(2a-d-2)(2a-d-6)(2a-d-8)} - 64b_R w_R \frac{a + 2^{4-a/2} - 10}{(a-2)(a-6)(a-8)}, \\ \beta_{w_R}(b_R, w_R) &= -(4-a)w_R - w_R^2 \frac{2a}{6-a} + b_R w_R \frac{2a}{6-d}.\end{aligned}\quad (4.26)$$

Performing a double  $\epsilon, \delta$  expansion and keeping terms up to linear in these parameters, we then have the RG functions:

$$\begin{aligned}\beta_b &= \epsilon b_R - 8b_R^2 - 4w_R^2 + 12b_R w_R, \\ \beta_w &= -\delta w_R - 4w_R^2 + 4b_R w_R.\end{aligned}\quad (4.27)$$

The fixed points  $b_R^*, w_R^*$  of the renormalization group transformations are defined as the common zeros of the RG functions (4.27). We find three distinct fixed points that determine the scaling behavior of the system in various regions of the  $a$  and  $d$  plane:

$$\text{Gaussian : } b_R^* = 0, w_R^* = 0, \quad \text{stable at } \epsilon, \delta < 0 \quad (4.28)$$

$$\text{Pure : } b_R^* = \frac{\epsilon}{8}, w_R^* = 0, \quad \text{stable at } \delta < \epsilon/2, \quad (4.29)$$

$$\text{LR : } b_R^* = \frac{\delta^2}{4(\epsilon - \delta)}, w_R^* = \frac{\delta(\epsilon - 2\delta)}{4(\delta - \epsilon)}, \quad \text{stable at } \epsilon/2 < \delta < \epsilon. \quad (4.30)$$

Here and below the index LR means that corresponding quantity is evaluated in the region of  $d, a$  plane, where the influence of long-range-correlated disorder is relevant.

We can also find estimates for critical exponents, governing the scaling of star polymers in solutions in the presence of correlated disorder. Making use of definition (3.3), recalling the expression or renormalized scale (4.14) and passing to the renormalized couplings we have:

$$\nu(b_R, w_R) = \frac{1}{2} + \frac{b_R}{2} - \frac{w_R}{2}. \quad (4.31)$$

Evaluating this expression at fixed points of the renormalization group transformation (4.28) - (4.30), we find the corresponding estimates for the size exponents:

$$\nu^{\text{Gaussian}} = \frac{1}{2}, \quad (4.32)$$

$$\nu^{\text{Pure}} = \frac{1}{2} + \frac{\epsilon}{16}, \quad (4.33)$$

$$\nu^{\text{LR}} = \frac{1}{2} + \frac{\delta}{8}. \quad (4.34)$$

Note that these exponents govern the scaling behavior of macromolecules in the regions of stability of the corresponding fixed points (4.28)-(4.30).

Similarly, evaluating (3.6) taking into account (4.10) one finds in terms of renormalized couplings:

$$\gamma(b_R, w_R) = 1 + \frac{b_R f(3-f)}{2} - \frac{w_R f(3-f)}{2}. \quad (4.35)$$

Again, evaluating this expression at the fixed points (4.28) - (4.30), we find:

$$\gamma_f^{\text{Gaussian}} = 1, \quad (4.36)$$

$$\gamma_f^{\text{Pure}} = \frac{1}{2} + \frac{\epsilon}{16} f(3-f), \quad (4.37)$$

$$\gamma_f^{\text{LR}} = \frac{1}{2} + \frac{\delta}{8} f(3-f). \quad (4.38)$$

At  $f = 1$  one restores corresponding exponents for a single polymer chain. Note, that the first-order expressions for the fixed point coordinates (4.28)-(4.30) and for the critical exponents (4.32)-(4.34) and (4.36)-(4.38) were obtained here for the annealed system. Thus, with  $\nu^{\text{LR}}$  and  $\gamma_f^{\text{LR}}$  as obtained in the regime of *annealed* disorder, we restore the corresponding exponents, governing the scaling of polymers in solutions in presence of *quenched* long-ranged correlated disorder, studied by us previously [31]. This supports the statement of equivalence between the annealed and quenched averaging when dealing with polymer systems.

Finally, we obtain estimates for the size ratio  $g = \frac{\langle R_{g\text{star}}^2 \rangle}{\langle R_{g\text{chain}}^2 \rangle}$  of star and linear polymers, recalling (4.21) and (4.22):

$$g(f) = \begin{cases} g^{\text{Gauss}}, & \varepsilon, \delta < 0, \\ g^{\text{Pure}}, & \delta < \varepsilon/2, \\ g^{\text{LR}}, & \varepsilon/2 < \delta < \varepsilon. \end{cases} \quad (4.39)$$

with:

$$g^{\text{Gauss}} = \frac{3f-2}{f^2}, \quad (4.40)$$

$$g^{\text{Pure}} = \frac{3f-2}{f^2} \left[ 1 - \frac{\varepsilon}{8} \left( \frac{13}{2} \frac{(f-1)(f-2)}{3f-2} - \ln(2) \frac{4(f-1)(3f-5)}{3f-2} + \ln(f) \right) \right], \quad (4.41)$$

$$g^{\text{LR}} = \frac{3f-2}{f^2} \left[ 1 - \frac{\delta}{4} \left( \frac{13}{2} \frac{(f-1)(f-2)}{3f-2} - \ln(2) \frac{4(f-1)(3f-5)}{3f-2} + \ln(f) \right) \right]. \quad (4.42)$$

With  $g^{\text{Pure}}$  we restore the size ratio for the case of polymers in pure solvent, evaluated previously in Refs. [16], [17].

## 5. Conclusions and Outlook

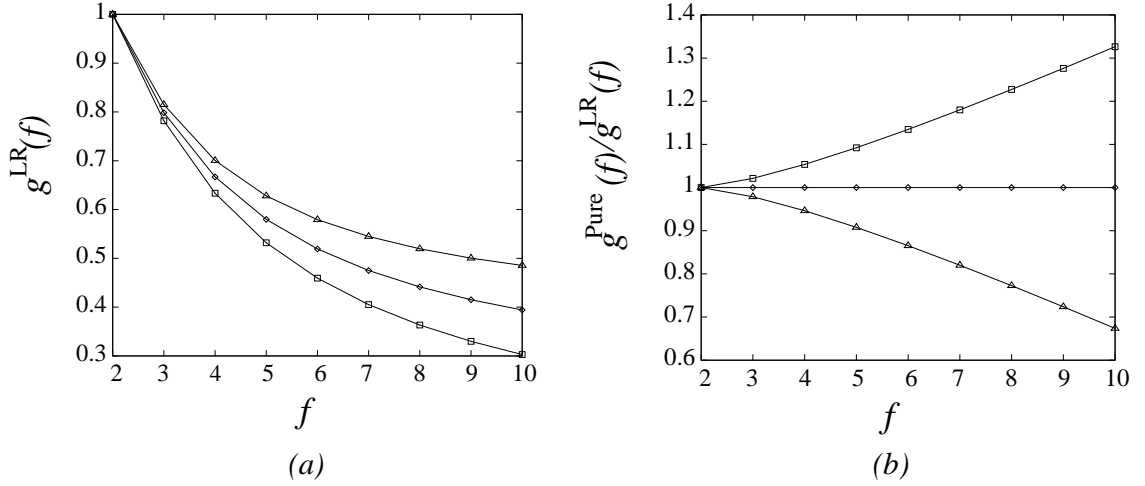
In the present paper, we have studied the impact of structural disorder on the static scattering function of  $f$ -arm star branched polymers in  $d$  dimensions. To this end, we consider the model of a star polymer immersed in a good solvent in presence of structural defects, correlated at large distances according to (1.6) with parameter  $a$  [30]. The impact of such long-range-correlated disorder on the scaling of linear and star branched polymers has been analyzed in our previous works [31]. Here, we are interested, in particular, in the ratio  $g(f)$  of scattering intensities of star and linear polymers of the same molecular weight, which is a universal experimentally measurable quantity (see (1.3)). We applied the direct polymer renormalization approach [1] and evaluate results within the double  $\varepsilon = 4 - d$ ,  $\delta = 4 - a$ -expansion.

Let us analyze the expressions obtained for the size ratio of star and linear polymers in solution in the presence of structural defects. First of all, as far as  $\delta = 4 - a$ -prefactor in (4.42) is positive for all  $f > 2$ , one immediately concludes, that the stronger the correlations of disorder (i.e. the larger is parameter  $\delta$ ), the larger is the size ratio  $g(f)$  and thus, the smaller is the distinction between the size measure of a star and linear polymers of the same molecular weight. In Fig. 6a, we present estimates for the size ratio (4.42) as a function of number of arms  $f$ , obtained by direct evaluation at several fixed values of the correlation parameter  $\delta$ . Besides an expected increase of  $g^{\text{LR}}(f)$  with growing  $\delta$  at each fixed  $f$ , we notice also a decrease of the size ratio with  $f$  for any fixed  $\delta$ . This can correspond to a shrinking of the effective radius of star polymers with increasing functionality.

Another interesting aspect results from comparing qualitatively the impact of long-range-correlated disorder on the size ratio with the impact of the excluded volume effect in pure solvent. We consider the ratio:

$$\frac{g^{\text{Pure}}(f)}{g^{\text{LR}}(f)} = 1 - \left( \frac{\varepsilon}{8} - \frac{\delta}{4} \right) \left( \frac{13}{2} \frac{(f-1)(f-2)}{3f-2} - \ln(2) \frac{4(f-1)(3f-5)}{3f-2} + \ln(f) \right). \quad (5.1)$$

In Fig. 6b, we present the evaluation of this ratio as function of  $f$  at three dimensions (taking  $\varepsilon = 1$ ) and several fixed values of correlation parameter  $\delta$ . Note, that correlated disorder with



**Figure 6.** Left: the size ratio (4.42) as a function of  $f$  at different values of correlation parameter  $\delta$ . From below:  $\delta = 0.1$ ,  $\delta = 0.5$ ,  $\delta = 1.0$ . Right: the ratio (5.1) as a function of  $f$  at different values of correlation parameter  $\delta$ . From above:  $\delta = 0.1$ ,  $\delta = 0.5$ ,  $\delta = 1.0$ . In both (a) and (b) we fix the value of parameter  $\varepsilon = 1$ .

$\delta = 0.5$  plays the role of “marginal”, separating a region where the ratio (5.1) increases with  $f$  (at  $\delta < 0.5$ ) and region where it decreases with  $f$  (any  $\delta > 0.5$ ).

Let us recall, that with the critical exponents  $\nu^{LR}$  (4.34) and  $\gamma_f^{LR}$  (4.38) that we obtained in the present paper in the regime of *annealed* disorder, we restore the corresponding exponents, governing the scaling of polymers in solutions in presence of *quenched* long-ranged correlated disorder, studied by us previously [31]. This supports the statement of equivalence between the annealed and quenched averaging when dealing with polymer systems. Thus our qualitative estimates for the size ratio of star and linear polymers in annealed correlated disorder (4.42) also holds for the case of quenched systems.

Note that our results are based on the first-order perturbation theory expansions and give rather qualitative description of the impact of structural disorder on the quantities of interest. To obtain the reliable quantitative estimates, the higher order analysis would be worthwhile, which is the subject of our forthcoming studies.

## Acknowledgements

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## Appendix

Here, as an example we evaluate the analytic expression corresponding to diagram (9) in Fig. 4 (shown in more details in Fig. 7), presenting contributions into radius of gyration of star polymer. We have for this contribution:

$$\overline{\langle e^{-i\vec{q}(\vec{r}_1(s_2) - \vec{r}_1(s_1))} \rangle}_{(9)} = -b_0 \int \mathcal{D}r e^{-\frac{1}{2} \sum_{i=1}^f \int_0^S ds \left( \frac{d\vec{r}_i(s)}{ds} \right)^2} e^{-i\vec{q}(\vec{r}_1(s_2) - \vec{r}_1(s_1))} \times$$

$$\int_{s_2}^S ds' \int_0^S ds'' \int d\vec{k} e^{-i\vec{k}(\vec{r}_1(s') - \vec{r}_2(s''))}.$$

Rewriting the last exponent:

$$-i\vec{k}(\vec{r}_1(s') - \vec{r}_2(s'')) = -i\vec{k}((\vec{r}_1(s') - \vec{r}_1(s_2)) + (\vec{r}_1(s_2) - \vec{r}_1(s_1)) + (\vec{r}_1(s_1) - \vec{r}_2(s''))), \quad (5.2)$$

and making use of (4.3)-(4.5), one arrives at:

$$\overline{\langle e^{-i\vec{q}(\vec{r}_1(s_2) - \vec{r}_1(s_1))} \rangle}_{(9)} = -b_0 \int \mathcal{D}r e^{-\frac{1}{2} \sum_{i=1}^f \int_0^S ds \left( \frac{d\vec{r}_i(s)}{ds} \right)^2} I_9(d) \quad (5.3)$$

with:

$$\begin{aligned} I_9(d) &\equiv \int_0^S ds'' \int_{s_2}^S ds' \int d\vec{k} e^{-\frac{k^2}{2}(s' - s_2 + s_1 + s'') - \frac{(\vec{q} + \vec{k})^2}{2}(s_2 - s_1)} = \\ &= e^{-\frac{q^2}{2}(s_2 - s_1)} \int_0^S ds'' \int_{s_2}^S ds' \int d\vec{k} e^{-\frac{k^2}{2}(s' + s'') - \vec{q}\vec{k}(s_2 - s_1)} = \\ &= (2\pi)^{-d/2} e^{-\frac{q^2}{2}(s_2 - s_1)} \int_0^S ds'' \int_{s_2}^S ds' (s'' + s')^{-d/2} e^{\frac{q^2}{2} \frac{(s_2 - s_1)^2}{(s' + s'')}}. \end{aligned} \quad (5.4)$$

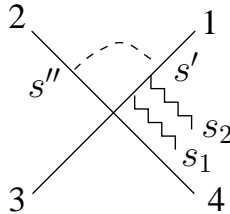
Taking the derivative over  $q$  according to (4.16) we receive:

$$\begin{aligned} \frac{\partial I_9(d)}{\partial q^2} \Big|_{q=0} &= (2\pi)^{-d/2} d(s_2 - s_1) \int_0^S ds'' \int_{s_2}^S ds' (s'' + s')^{-d/2} - \\ &- (2\pi)^{-d/2} d(s_2 - s_1)^2 \int_0^S ds'' \int_{s_2}^S ds' (s'' + s')^{-d/2-1} = \\ &(2\pi)^{-d/2} \frac{d(s_2 - s_1)}{(1 - d/2)(2 - d/2)} \left[ (2S)^{2-d/2} - (S + s_2)^{2-d/2} - S^{2-d/2} + s_2^{2-d/2} \right] - \\ &- (2\pi)^{-d/2} \frac{d(s_2 - s_1)^2}{(1 - d/2)(-d/2)} \left[ (2S)^{1-d/2} - (S + s_2)^{1-d/2} - S^{1-d/2} + s_2^{1-d/2} \right]. \end{aligned} \quad (5.5)$$

Finally, the contribution into the gyration radius (4.15) can be found by integrating over  $s_1, s_2$ . Note, that the Gaussian integral in (5.3) cancels against the numerator, when averaging (4.12) is performed.

The expressions corresponding to other diagrams in Fig. 4 are listed below (note, that  $I(d)$  and  $I(a)$  arise, correspondingly, when treating interactions with couplings  $b_0$  and  $w_0$  respectively). The factors  $(2\pi)^{-d/2}$  and  $(2\pi)^{-a/2}$  in front of each integral are omitted.

$$I_1(d) = e^{-\frac{q^2}{2}(s_2 - s_1)} \int_{s_2}^S ds'' \int_{s_1}^{s_2} ds' (s'' - s')^{-d/2} e^{\frac{q^2}{2} \frac{(s_2 - s')^2}{(s'' - s')}} ,$$



**Figure 7.** Example of diagrammatic contribution into the radius of gyration of star polymer (4.15).

$$\begin{aligned}
 I_2(d) &= e^{-\frac{q^2}{2}(s_2-s_1)} \int_{s_1}^{s_2} ds'' \int_0^{s_1} ds' (s'' - s')^{-d/2} e^{\frac{q^2}{2} \frac{(s''-s_1)^2}{(s''-s')}} \\
 I_3(d) &= e^{-\frac{q^2}{2}(s_2-s_1)} \int_{s_2}^S ds'' \int_0^{s_1} ds' (s'' - s')^{-d/2} e^{\frac{q^2}{2} \frac{(s_2-s_1)^2}{(s''-s')}} , \\
 I_4(d) &= e^{-\frac{q^2}{2}(s_2-s_1)} \int_{s_2}^S ds'' \int_{s_2}^{s''} ds' (s'' - s')^{-d/2} , \\
 I_5(d) &= e^{-\frac{q^2}{2}(s_2-s_1)} \int_0^{s_1} ds'' \int_0^{s''} ds' (s'' - s')^{-d/2} , \\
 I_6(d) &= e^{-\frac{q^2}{2}(s_2-s_1)} \int_{s_1}^{s_2} ds'' \int_{s_1}^{s''} ds' (s'' - s')^{-d/2} e^{\frac{q^2}{2}(s''-s_1)} , \\
 I_7(d) &= e^{-\frac{q^2}{2}(s_2-s_1)} \int_0^S ds'' \int_0^{s_1} ds' (s'' + s')^{-d/2} \\
 I_8(d) &= e^{-\frac{q^2}{2}(s_2-s_1)} \int_0^S ds'' \int_{s_1}^{s_2} ds' (s'' + s')^{-d/2} e^{\frac{q^2}{2} \frac{(s'-s_1)^2}{(s'+s'')}} , \\
 I_9(d) &= e^{-\frac{q^2}{2}(s_2-s_1)} \int_0^S ds'' \int_{s_2}^S ds' (s'' + s')^{-d/2} e^{\frac{q^2}{2} \frac{(s_2-s_1)^2}{(s'+s'')}} , \\
 I_{10}(d) &= e^{-\frac{q^2}{2}(s_2-s_1)} \int_0^S ds'' \int_0^S ds' (s'' + s')^{-d/2} , \\
 I_{11}(d) &= e^{-\frac{q^2}{2}(s_2-s_1)} \int_0^S ds'' \int_0^{s''} ds' (s'' - s')^{-d/2} , \\
 I_{12}(d) &= e^{-\frac{q^2}{2}(s_2+s_1)} \int_{s_1}^S ds'' \int_{s_1}^{s''} ds' (s'' - s')^{-d/2} , \\
 I_{13}(d) &= e^{-\frac{q^2}{2}(s_2+s_1)} \int_{s_1}^S ds'' \int_0^{s_1} ds' (s'' - s')^{-d/2} e^{\frac{q^2}{2} \frac{(s_1-s')^2}{(s''-s')}} , \\
 I_{14}(d) &= e^{-\frac{q^2}{2}(s_2+s_1)} \int_0^{s_1} ds'' \int_0^{s''} ds' (s'' - s')^{-d/2} e^{\frac{q^2}{2}(s''-s')} , \\
 I_{15}(d) &= e^{-\frac{q^2}{2}(s_2+s_1)} \int_{s_2}^S ds'' \int_{s_1}^S ds' (s'' + s')^{-d/2} e^{\frac{q^2}{2} \frac{(s_1+s_2)^2}{(s''+s')}} ,
 \end{aligned}$$

$$\begin{aligned}
I_{16}(d) &= e^{-\frac{q^2}{2}(s_2+s_1)} \int_0^{s_2} ds'' \int_{s_1}^S ds' (s'' + s')^{-d/2} e^{\frac{q^2}{2} \frac{(s_1+s'')^2}{(s''+s')}}, \\
I_{17}(d) &= e^{-\frac{q^2}{2}(s_2+s_1)} \int_0^{s_2} ds'' \int_0^{s_1} ds' (s'' + s')^{-d/2} e^{\frac{q^2}{2}(s''+s')}, \\
I_{18}(d) &= e^{-\frac{q^2}{2}(s_2+s_1)} \int_0^S ds'' \int_0^{s_2} ds' (s'' + s')^{-d/2} e^{\frac{q^2}{2} \frac{(s')^2}{(s''+s')}}, \\
I_{19}(d) &= e^{-\frac{q^2}{2}(s_2+s_1)} \int_{s_2}^S ds'' \int_0^S ds' (s'' + s')^{-d/2} e^{\frac{q^2}{2} \frac{(s_2)^2}{(s''+s')}}, \\
I_{20}(d) &= e^{-\frac{q^2}{2}(s_2+s_1)} \int_0^S ds'' \int_0^{s''} ds' (s'' - s')^{-d/2}, \\
I_{21}(d) &= e^{-\frac{q^2}{2}(s_2+s_1)} \int_0^S ds'' \int_0^S ds' (s'' + s')^{-d/2}.
\end{aligned}$$

## References

- desCloizeaux J., Jannink G., Polymers in Solution: Their Modeling and Structure. Clarendon Press, Oxford, 1990.
- Roovers J.E.L., Bywater S., Macromolecules, 1972, **5**, 384.
- Roovers J., Hadjichristidis N., Fetters L.J., Macromolecules, 1983, **16**, 214.
- Huber K., Burchard W., Fetters L.J., Macromolecules, 1984, **17**, 541.
- Khasat N., Pennisi R.W., Hadjichristidis N., Fetters L.J., Macromolecules, 1988, **21**, 1100.
- Bauer B.J., Fetters L.J., Graessley W.W., Hadjichristidis N., Quack G.F., Macromolecules, 1989, **22**, 2337.
- Merkle G., Burchard W., Lutz P., Freed K.F., Gao J., Macromolecules, 1993, **26**, 2736.
- Grest G.S., Fetters L.J., Huang J.S., Richter D., Advan. Chem. Physics, 1996, **94**, 67.
- Likos C.N., Phys. Rep., 2001, **348**, 267.
- von Ferber C., Holovatch Yu., eds., Special Issue "Star Polymers". Vol. 5 of Condens. Matter Phys., 2002.
- Duplantier B., J. Stat. Phys., 1989, **54**, 581.
- Schäfer L., von Ferber C., Lehr U., Duplantier B., Nucl. Phys. B, 1992, **374**, 473.
- Likos C.N., Harreis H.M., Condens. Matter Phys., 2002, **5**, 173; Likos C. N., Löwen H., Watzlawek M., Abbas B., Jucknischke O., Allgaier J., Richter D., Phys. Rev. Lett., 1998, **80** 4450.
- Zimm B.H., Stockmayer W.H., J. Chem. Phys., 1949, **17**, 1301.
- Daoud M., Cotton J.P., J. Phys., 1982, **43**, 531.
- Miyake A., Freed K.F., Macromolecules, 1983, **16**, 1228; Macromolecules, 1984, **17**, 678.
- Alessandrini J.L., Carignano M.A., Macromolecules, 1992, **25**, 1157.
- Whittington S.G., Lipson J.E.G., Wilkinson M.K., Gaunt D.S., Macromolecules, 1986, **19**, 1241.
- Grest G., Kremer K., Wittington T.A., Macromolecules, 1987, **20**, 1316.
- Batoulis J., Kremer K., Macromolecules, 1989, **22**, 4277.
- Bishop M., Clarke J.H.R., Freire J.J., J. Chem. Phys., 1993, **98**, 3452.
- Wei G., Macromolecules, 1997, **30**, 2125.
- Pusey P.N., van Megen W., Nature, 1986, **320**, 340.
- Cannell D.S., Rondelez F., Macromolecules, 1980, **13**, 1599.
- Dullen A.L., Porous Media: Fluid Transport and Pore Structure. Academic, New York, 1979.
- Goodesel D.S., Trends Biochem. Sci., 1991, **16** 203; Horwitch A., Nature, 2004, **431**, 520; Minton A., J. Biol. Chem., 2001, **276**, 10577.
- Kim Y., J. Phys. C, 1983, **16**, 1345.



28. Nakanishi H., Lee S.B., J. Phys. A, 1991, **24**, 1355; Lee S.B., Nakanishi H., Phys. Rev. Lett., 1988, **61**, 2022.
29. Sahimi M., Flow and Transport in Porous Media and Fractured Rock. VCH, Weinheim, 1995.
30. Weinrib A., Halperin B.I., Phys. Rev. B, 1983, **27**, 413.
31. Blavats'ka V., von Ferber C., Holovatch Yu., Phys. Rev. E, 2001, **64** 041102; Phys. Rev. E, 2006, **74**, 031801.
32. Brout R., Phys. Rev., 1959, **115**, 824; Folk R., Holovatch Yu., and Yavors'kii T., Physics-Uspekhi, 2003, **46**, 169; see also the review papers in volume series "Order, Disorder and Criticality. Advanced Problems of Phase Transition Theory (ed. Yu. Holovatch)", (World Scientific, Singapore, vol. 1 (2004), vol. 2 (2007), vol. 3 (2012), to appear).
33. Cherayil B.J., J. Chem. Phys., 1990, **92**, 6246.
34. Wu D., Hui K., Chandler D., J. Chem. Phys., 1991, **96**, 835.
35. Ippolito I., Bideau D., Hansen A., Phys. Rev. E, 1998, **57**, 3656.
36. Patel D.M., Fredrickson G.H., Phys. Rev. E, 2003, **68**, 051802.
37. Baumgärtner A., Muthukumar M., Adv. in Chem. Phys., 1996, **94**, 625.
38. Zinn-Justin J., Phase Transitions and Critical Phenomena. Oxford University Press, Oxford, 1996; Kleinert H., Schulte-Frohlinde V., Critical Properties of  $\varphi^4$ -Theories. World Scientific, Singapore, 2011; Amit D.J., Field Theory, the Renormalization Group, and Critical Phenomena. World Scientific, Singapore, 1984.

## Вплив безладу на статичну функцію розсіювання зіркових полімерів

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Представлено аналіз впливу структурного безладу на статичну функцію розсіювання  $f$ -гілкового зіркового полімера у  $d$ -вимірному просторі. Розглянуто модель зіркового полімера у хорошому розчиннику в присутності структурних дефектів, скорельованих на великих віддальх  $r$  згідно степеневому закону  $\sim r^{-a}$ . Зокрема, ми цікавимося відношенням  $g(f)$  інтенсивностей розсіювання зіркового та лінійного полімерів однакової молекулярної маси, що є універсальною, експериментально спостережуваною величиною. Ми застосовуємо метод прямого полімерного перенормування і використовуємо подвійний  $\varepsilon = 4 - d$ ,  $\delta = 4 - a$ -розклад. Знайдено зростання величини  $g(f)$  із зростанням параметра  $\delta$ . Таким чином, зростання кореляцій безладу приводить до зменшення відмінності між розміром зіркових та лінійних полімерів із однаковою молекулярною вагою.

Ключові слова: полімери, структурний безлад, універсальність, ренормалізаційна група

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